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Many-body effects in the stimulated Raman response of binary mixtures: A comparison between theory and experiment

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The subpicosecond dynamics of binary mixtures of carbon disulfide and alkane have been studied using third-order time-resolved Raman techniques. Both the anisotropic and the isotropic responses were investigated. These depend differently on many-body contributions to the first-order susceptibility and probe different modes in the liquid. The anisotropic response is dominated by single molecule effects, whereas the isotropic response is completely determined by many-body contributions since the single molecule response vanishes. To interpret the experimental results, molecular dynamics simulations were performed on model mixtures. The effect of dilution on the subpicosecond response cannot be explained by many-body effects in the first-order susceptibility alone. Aggregation due to permanent quadrupole moments on the carbon disulfide molecules and density changes upon dilution are also inadequate explanations for the observed effect. Apparently the character of the many-body dynamics itself is modified by the change of the molecular force fields, when carbon disulfide molecules are replaced by alkanes. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1475763]

I. INTRODUCTION

Femtosecond laser spectroscopy techniques are powerful methods to study the ultrafast dynamics in liquids. Experiments such as the (heterodyned) optical Kerr effect[1–3] and transient grating scattering[4,5] allow the observation of induced motions in real time rather than as resonances. For a molecule to be Raman active the polarizability has to be coordinate dependent. In anisotropic molecules the polarizability depends on the orientational coordinate of the molecules and hence a rotational Raman response is observed. In the liquid phase this response will be highly-influenced by the many-body interaction between the individual rotating molecule and the surrounding molecules. The many-body interactions result in line broadening of the response in the frequency domain, corresponding to an, often exponentially, decaying tail in the time domain.

The molecular polarizability itself is also affected by the presence of other polarizable molecules in the neighborhood, due to local field effects. In liquids, the Raman response is therefore also determined by the coordinate dependence of the many-body (macroscopic) counterpart to the polarizability, i.e., the first-order susceptibility. Now, not only the individual single molecule coordinates but also the intermolecular coordinates become important. The many-body effects in the first-order susceptibility give rise to response due to dynamics in the local structure, allowing observations of collisions, collective movements and structural effects.

The influence of many-body interactions on the first-order susceptibility can be investigated through dilution studies. Such studies provide information not only on the many-body dynamics and the local field effects in the liquid, but also on the structure of the diluted liquid. The formation of clusters of molecules in the mixture will tend to preserve the response from many-body effects in the first-order susceptibility, whereas a solvent effectively isolating the polarizable molecules from each other will suppress this part of the response to some extent.

Various liquid mixtures have been investigated experimentally using third-order nonlinear Raman response techniques to probe the ultrafast dynamics.[1–3,6–12] Diluted carbon disulfide belongs to one of the most studied systems because of the intense anisotropic response of this molecule. Studies of carbon disulfide have been done in mixtures with alkanes,[2,3,6,7] chlorine substituted methane[1,10,11] and various alcohols.[11] Also molecular dynamics (MD) simulations were performed previously on mixtures of carbon disulfide and carbon tetrachloride,[13,14] but to our knowledge no calcula-

tions have been reported of the third-order nonlinear Raman response of liquid mixtures.

The anisotropic third-order nonlinear Raman response can be roughly separated into three main features, i.e., the diffusive, the interaction-induced and the librational response. The diffusive response is caused by the diffusive realignment of single molecules. Only this contribution can be clearly recognized because of its distinct and slow exponential decay. The interaction-induced response is originating from intermolecular motions getting intensity from the dipole-induced dipole effects (local field effects) and higher multipole and collision effects.[15] The librational response comes from single molecules moving in the local potential of neighboring molecules.

The isotropic third-order nonlinear Raman response is in general much weaker than the anisotropic response. It is solely due to the interaction induced effects. Very few investigations have been done on the isotropic response,[16–19] despite of the fact that it provides an opportunity to investigate many-body effects without the disturbing influence of the single molecule response. The obvious reason for avoiding the isotropic response has been its very low intensity.

All investigations on mixtures until now have been interpreted in terms of analytical models at a macroscopic level of theory, assigning the nondiffusional response either to librational degrees of freedom[1,2,6] or interaction induced response.[11] These approaches were based on an interpretation in phenomenological terms, such as homogeneous or inhomogeneous broadening of the Raman response or an atomic collision model, originally proposed for low density media.[20] Recently a macroscopic model was presented[21] that describes the diffusional and nondiffusional response in terms of abstract oscillators in which the microscopic many-body dynamics is summarized.

Getting an understanding of the optical response on a microscopic (molecular) scale in terms of molecular properties such as force fields, atomic masses and polarizabilities would be preferable. Using MD simulations one can perform studies on real systems to get insight into the effects of dilution on a microscopic scale. This is particular valuable when these results are compared to experimental investigations of how changes in the local environment of molecules affect the many-body part of the Raman signals.

In this paper the effect of dilution is investigated for binary mixtures of carbon disulfide with various alkanes. The anisotropic and the isotropic responses are examined both experimentally and theoretically. In Sec. II the theory used to analyze the data is developed and in Sec. III the experiments are described. The experimental results are compared with theory and molecular dynamics simulations of an idealized mixture in Sec. IV, together with a discussion of possible explanations of the deviations. The conclusions are presented in Sec. V.

II. THEORY

The change of the nonlinear Raman spectrum upon dilution will be considered for the simple case, where the dynamics of the system does not change upon dilution. Furthermore, it will be assumed that only one of the two components in the mixture contributes to the Raman response. The interaction induced contribution to the susceptibility will be treated within the first-order approximation to the dipole-induced dipole model. In this model the effective molecular polarizabilities, when local fields are present, are given by[22–25]

$$\mathbf{\Pi}_i^{(1)} = \alpha_i + \alpha_i \sum_{j \neq i} \mathbf{T}_{ij} \alpha_j + \frac{4\pi \langle \chi^{(1)} \rangle}{3} \alpha_i . \tag{1}$$

Here α_i is the single molecule polarizability tensor, $\mathbf{T}_{ij}$ is the dipole tensor, and $\langle \chi^{(1)} \rangle$ is the constant average susceptibility. The first-order (linear) approximation is used here to provide insight into the physics of interaction-induced optical response. When performing actual calculations of the response (see Sec. IV), the full DID effect will be taken into account.

The first-order dipole-induced dipole polarizability is the response to the macroscopic electric field inside a dielectric medium and not to the external electric field, eliminating sample shape dependent effects. This means that the molecules feel the local field generated by a dielectric medium in the total space around them. This is the first term of Eq. (1). The dipole-induced dipole coupling in the local surrounding of a molecule will be taken into account explicitly through the second term of Eq. (1). The volume in which this is done we will call the cavity. Since the coupling is calculated explicitly in this volume, a term has to be subtracted that contains the effect of the dielectric medium inside the cavity. This is the third term in Eq. (1).

The full dipole-induced dipole effect is accounted for if in the second term of Eq. (1) the polarizability α_j of the molecules generating the local fields on the considered molecule i is replaced by the effective polarizability $\mathbf{\Pi}_j$. This takes into account that the dipole on molecule j is also induced by a local field. The set of equations will then have to be solved self-consistently.[22–25] As mentioned above, in the MD calculations that will be reported in Sec. IV, this self-consistency was fully taken into account.

To shorten the notation the induced polarizability $\alpha_i \mathbf{T}_{ij} \alpha_j$ will be abbreviated with $\mathbf{D}_{ij}$. The instantaneous susceptibility in an ensemble is given by the ensemble average of the effective polarizabilities

$$\chi^{(1)} = \frac{1}{V} \sum_i \left(\alpha_i + \sum_{j \neq i} \mathbf{D}_{ij} + \frac{4\pi \langle \chi^{(1)} \rangle}{3} \alpha_i \right), \tag{2}$$

where V is the ensemble volume.

The third-order Raman response is given by the time correlation function[24,26–28]

$$\chi^{(3)}_{abcd}(t) = -\frac{1}{2kT} \langle \dot{\chi}^{(1)}_{ab}(t) \chi^{(1)}_{cd}(0) \rangle . \tag{3}$$

Substituting the instantaneous susceptibility Eq. (2) into this equation reveals six types of terms, which will be denoted RA, DI, CA, C1, C2, and C3, respectively. These we will now describe one at a time, omitting the proportionality factor $-(1/2kTV^2)$ and the indices for the polarization directions.

The single molecule realignment term (RA) is proportional to

$$R^{\mathrm{RA}}(t)=\sum_{i,j}\langle\dot{\alpha}_i(t)\alpha_j(0)\rangle$$
$$=\sum_i\langle\dot{\alpha}_i(t)\alpha_i(0)\rangle+\sum_i\sum_{j\neq i}\langle\dot{\alpha}_i(t)\alpha_j(0)\rangle$$
$$=\sum_i\langle\dot{\alpha}_i(t)\alpha_i(0)\rangle. \tag{4}$$

This term only depends on the rotational motion of single molecules, since the derivative of the correlation between the molecular polarizabilities of two randomly chosen different molecules, in the second term on the second line, vanishes.

The dipole interaction terms (DI) are proportional to

$$R^{\mathrm{DI}}(t)$$
$$=\sum_{i,k}\sum_{\substack{j\neq i\\ l\neq k}}\langle\dot{D}_{ij}(t)D_{kl}(0)\rangle$$
$$=\sum_i\sum_{j\neq i}(\langle\dot{D}_{ij}(t)D_{ij}(0)\rangle+\langle\dot{D}_{ij}(t)D_{ji}(0)\rangle)$$
$$+\sum_i\sum_{j\neq i}\sum_{k\neq i,j}\begin{pmatrix}\langle\dot{D}_{ij}(t)D_{ik}(0)\rangle+\langle\dot{D}_{ij}(t)D_{ki}(0)\rangle\\ +\langle\dot{D}_{ij}(t)D_{kj}(0)\rangle+\langle\dot{D}_{ij}(t)D_{jk}(0)\rangle\end{pmatrix}$$
$$+\sum_i\sum_{j\neq i}\sum_{k\neq i,j}\sum_{l\neq i,j,k}\langle\dot{D}_{ij}(t)D_{kl}(0)\rangle. \tag{5}$$

The last term vanishes, because the correlation between the dipole interaction on two independent pairs of molecules does not vary in time.

The cross terms between the single molecule realignment and the dipole interaction (C1) are proportional to

$$R^{\mathrm{C1}}(t)=\sum_{i,k}\sum_{j\neq i}(\langle\dot{\alpha}_k(t)D_{ij}(0)\rangle+\langle\dot{D}_{ij}(t)\alpha_k(0)\rangle)$$
$$=\sum_i\sum_{j\neq i}(\langle\dot{\alpha}_i(t)D_{ij}(0)\rangle+\langle\dot{\alpha}_i(t)D_{ji}(0)\rangle$$
$$+\langle\dot{D}_{ij}(t)\alpha_i(0)\rangle+\langle\dot{D}_{ji}(t)\alpha_i(0)\rangle)$$
$$+\sum_i\sum_{j\neq i}\sum_{k\neq i,j}(\langle\dot{\alpha}_i(t)D_{jk}(0)\rangle+\langle\dot{D}_{jk}(t)\alpha_i(0)\rangle)$$
$$=\sum_i\sum_{j\neq i}(\langle\dot{\alpha}_i(t)D_{ij}(0)\rangle+\langle\dot{\alpha}_i(t)D_{ji}(0)\rangle$$
$$+\langle\dot{D}_{ij}(t)\alpha_i(0)\rangle+\langle\dot{D}_{ji}(t)\alpha_i(0)\rangle). \tag{6}$$

Here the last equality is based on the fact that the correlation between the polarizability (α_i) on one molecule and the polarizability on a second one induced by yet another molecule (D_{jk}) is constant in time.

The remaining contributions to the third-order Raman response arise from correlations with the last term of Eq. (2). This term eliminates the effect from a dielectric medium inside the cavity since the dipole-induced dipole coupling is explicitly taken into account in that volume. All of these contributions can be expressed in terms of the single molecule polarizabilities in Eqs. (4) and (6), scaled with a factor $4\pi\langle\chi^{(1)}\rangle/3$ or $(4\pi\langle\chi^{(1)}\rangle/3)^2$. The cavity correction term (CA) is given by

$$R^{\mathrm{CA}}(t)=\left(\frac{4\pi\langle\chi^{(1)}\rangle}{3}\right)^2\sum_i\langle\dot{\alpha}_i(t)\alpha_i(0)\rangle. \tag{7}$$

The single molecule realignment-cavity correction cross term (C2) is given by

$$R^{\mathrm{C2}}(t)=2\frac{4\pi\langle\chi^{(1)}\rangle}{3}\sum_i\langle\dot{\alpha}_i(t)\alpha_i(0)\rangle. \tag{8}$$

And finally the cross term between the dipole interaction and the cavity correction terms (C3) is given by

$$R^{C3}(t)$$
$$=\frac{4\pi\langle\chi^{(1)}\rangle}{3}\sum_i\sum_{j\neq i}\begin{pmatrix}\langle\dot{\alpha}_i(t)D_{ij}(0)\rangle+\langle\dot{\alpha}_i(t)D_{ji}(0)\rangle\\ +\langle\dot{D}_{ij}(t)\alpha_i(0)\rangle+\langle\dot{D}_{ji}(t)\alpha_i(0)\rangle\end{pmatrix}. \tag{9}$$

Dilution can be looked upon as replacing Raman active molecules with molecules that do not contribute to the Raman response. Removing active chromophores from the solution is equivalent to reducing the summations in Eqs. (4)–(9). From the single summation in the last line of Eq. (4) it can be seen that the single molecule realignment part of the response scales linearly with the concentration. The C1 cross term that depends on the correlation between the rotational motion of a molecule and a dipole interaction involving the same molecule consist of a double summation and is growing quadratic with the concentration. The dipole interaction term (DI) involves both a double and a triple summation, giving rise to quadratic and cubic growth, respectively.

In the terms involving the cavity correction (CA, C2, and C3), as a first approximation the constant average susceptibility $\langle\chi^{(1)}\rangle$ can be taken to be proportional to the concentration. Consequently these terms scale quadratic (C2) and cubic (C3 and CA), with the concentration, respectively. These three last contributions should be seen as corrections to the terms involving the dipole interaction, since the cavity correction ensures that the dielectric medium inside the cavity, where the interactions are taken explicitly into account through the dipole interaction scheme, is not counted twice.

This analysis suggests that in general terms scaling linear, quadratic and cubic in the concentration upon dilution can be found. It should be mentioned that by the use of the first-order DID model instead of the full self-consistent DID model terms are omitted that also scale with quadratic and higher powers, but only the single molecule realignment term scales linearly.

Some of the terms found can sometimes be excluded by using symmetry arguments. For instance, the terms including single molecule polarizabilities are vanishing in the isotropic response since the trace of the single molecule polarizability is constant as long as intramolecular vibrational motion can

be neglected. The isotropic response is then dominated by the terms in Eq. (5), scaling quadratic and cubic in the concentration.

In a real mixture, the ideal conditions considered till now will never be found. Structural, dynamical and chemical changes of the liquid can take place upon dilution. Differences in molecular shapes and sizes of the two components will change the structure and dynamics of the liquid. Furthermore, the differences in the weak forces, binding the molecules together in the liquid, might change the structure and dynamics as well. For instance, in mixtures of water and ethanol the structural changes due to redistribution of hydrogen bonds result in a considerable decrease of the molar volume. In liquids with weaker bonding types, similar effects will take place but on a smaller scale. In some cases, specific intermolecular forces can also have drastic effects. Dimers, clusters, micelles, and molecular aggregates are examples of systems where individual molecules associate with each other. Such molecular structures can be expected to be relatively stable upon dilution and they will often give rise to distinctively different optical responses than unassociated single molecules. Chemical reactions in the mixture, giving rise to breaking or formation of covalent bonds, will of course also change the response considerably.

In general the optical signals are strongly dependent on the concentration of Raman active molecules. The growth rate depends on how many individual molecules are needed to produce the response. Only one Raman active molecule is needed in the single molecule reorientational response (RA), while at least two molecules are involved in the interaction induced parts of the response leading to quadratic or higher order dependence in the concentration.

To get a picture of the terms that are determining the Raman response, molecular dynamics simulations on diluted systems using the full DID model,[22–25] were performed. Thus, the information content of the experiments concerning the structural dynamics of liquids can be evaluated. In such simulations a fraction of the molecules can be made invisible and excluded from the susceptibility calculations. This is identical to reducing the sums in Eqs. (4)–(9). In this way an ideal solution is obtained, where the structure and dynamics of the system is maintained during the process of dilution.

The ideal mixture will thus be a mixture of two almost identical molecules. Experimental deviation from ideal behavior will provide valuable information on the different properties of the two types of molecules and about their respective interactions. Investigations on a wider range of mixtures can provide valuable information on molecular interactions in general.

III. EXPERIMENT

Kerr effect and transient grating scattering experiments were employed to study the third-order time resolved Raman response of carbon disulfide and carbon disulfide/alkane binary mixtures.

The OHD-Kerr experiments were performed as proposed by McMorrow *et al.*[1] Briefly, we used a Ti:sapphire oscillator (Mai Tai, Spectra-Physics) delivering $\sim$70 fs pulses centered around 800 nm at an 82 MHz repetition rate. After pre-compression in a fused silica prism pair, the pulses with an energy of 7 nJ/pulse were split into pump and probe beams with a ratio 10:1, respectively. The probe pulse was variably delayed by a computer controlled delay stage. The pump and probe beams, polarized at 45° with respect to each other, were focussed into a sample by using a spherical mirror of $r=25$ cm. The necessary pump and probe polarization orientations were set by 3 mm thick Glan–Taylor polarizers and a $\lambda/2$ plate in the pump beam. A 90° out-of-phase local oscillator field for the signal was generated by insertion of a $\lambda/4$ plate in the probe beam and detuning of the probe polarizer by $\sim$1.5°. By measuring the cross-correlation function of the pump and probe beams in a 20 μm BBO crystal and applying a deconvolution procedure in frequency domain,[29,30] the distortions introduced by the instantaneous electronic response were separated from the (delayed) response due to the induced nuclear dynamics in the liquid.

The transient grating experiments in BOXCAR geometry were performed by using a 1 kHz Ti:sapphire laser system (Hurricane, Spectra-Physics) and optical parametric amplifier (OPA). The laser system produces 120 fs, 800 μJ pulses at 1 kHz centered at 800 nm. About $\sim$300 μJ pulses were split off to pump a traveling wave optical parametric amplifier (TOPAS, Light Conversion, Ltd.). The sample was excited with pulses centered at a wavelength of 700 nm (second harmonics of the signal wave of the TOPAS at 1400 nm). Before splitting into two pump and a probe beam, the output was compressed to $\sim$50 fs in a double-pass compressor based on two fused silica prisms. In addition to pulse shortening, the compressor allows spatial separation of the different spectral components of the parametric light (signal and idler beams). The pulse shape was determined by frequency resolved optical gating (FROG).[31,32] The experiments were performed with pulses, attenuated to an energy of $<$15 nJ per pulse. After setting the polarization of the beams by $\lambda/2$ plates and 3 mm thick Glan–Taylor polarizers, they were focussed into the sample with a spherical mirror of $r=25$ cm. Different tensor elements of the third-order nonlinear optical response function $\chi^{(3)}_{ijkl}$ can be determined by varying the polarizations of the interacting beams as well as selecting a polarization direction in the detection. The signal was filtered by a Glan–Taylor polarizer, detected by a silicon photodiode, processed by lock-in amplifier, digitized and stored in a computer for further analysis.

The samples consisted of binary mixtures of CS_2 and alkane solvents (pentane, heptane, and decane) placed in a 1 mm standing quartz cell. To avoid heating effects the sample was stirred with a glass-coated metal stirrer placed inside the cell and a rotating magnet. CS_2 as well as pentane, heptane, and decane (all spectroscopic grade) were obtained from Merck and Lab-Scan and used without further purification. In order to remove dust particles the solvents were filtered by using 0.2 μm pore size filters directly before injection into the cell.

IV. RESULTS AND DISCUSSION

The third-order Raman response was calculated using MD for idealized diluted carbon disulfide. These mixtures, as

TABLE I. Density, viscosity, and refractive index of the pure liquids at 20 °C (Ref. 40). The concentration of CS_2 molecules in the mixture with alkanes is given at the volume percentage.

Liquid	ρ (g/ml)	η (cP)	n_D
Pentane	0.6262	0.240	1.3575
Heptane	0.6837	0.409	1.3878
Decane	0.7300	0.92	1.4102
CS_2	1.2632	0.363	1.6319

already described in Sec II, consist of chromophore carbon disulfide molecules that contribute to the optical response, and so-called ghost carbon disulfide molecules. These latter ones do not contribute to the Raman response but fill out the void between the chromophores and preserve the dynamic behavior of the liquid. We choose to calculate such an idealized diluted sample rather than a specific mixture in order to obtain general information on the effects of dilution upon many-body effects. The deviations from this model, that are observed in experimental results, can then be directly related to specific physical effects that provide information on the microscopic structure and dynamics of the liquid.

The time correlation function method[24,26] was employed to calculate the response function from the dynamics, which was simulated using the conditions described in our earlier paper.[28] A common literature force field[33] of atomic Lennard-Jones type was used,

$$V_{\mathrm{LJ}}=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]. \tag{10}$$

Here ϵ is the depth of the potential well and σ a characteristic distance. The simulations were done with 64 and 256 molecule simulation boxes in 5 ns trajectories. The degree of dilution was set by varying the relative number of chromophores with polarizabilities and ghost molecules without polarizabilities.

The experiments were performed on mixtures of carbon disulfide and the alkanes pentane, heptane, and decane. Some of the important physical properties of the pure liquids are listed in Table I. The mixtures have been prepared with volume fractions of carbon disulfide of 30%, 50%, 70%, and 100% for the anisotropic OHD-Kerr experiments and from 0 to 100% with 10% intervals for the isotropic transient grating experiments.

In the OHD-Kerr experiment, used to measure the anisotropic response, the sample is excited by two pump fields originating from the same laser pulse. After a time delay the signal is measured as the induced rotation of the polarization. The observed signal for pure CS_2 is shown in Fig. 1. At zero time delay an instantaneous response of electronic origin is observed, followed by a rising nuclear signal. After reaching its maximum, the signal starts to decay, first nonexponentially and later in an exponential way. The electronic part of the response can be eliminated together with the pulse shape dependence by deconvolution of the signal,[29,30] so that the pure impulsive nuclear anisotropic response is obtained.

In the transient grating experiments, two different pump beams are used to induce a grating in the sample from which a delayed prope pulse is Bragg scattered. For parallel polarized pump pulses and prope and detection polarizations at magic angle, the isotropic response is measured. The signal measured for pure CS_2 is shown in Fig. 1. An instant electronic response is observed as well as a weak isotropic nuclear response with finite rise time. In principle the electronic response can be removed using a deconvolution procedure,[34] but if the nuclear signal is very weak, noise introduced by this procedure will severely contaminate the signal. Therefore the deconvolution procedure has not been applied. Instead, the isotropic response was only examined at long time delays, where the electronic response vanishes.

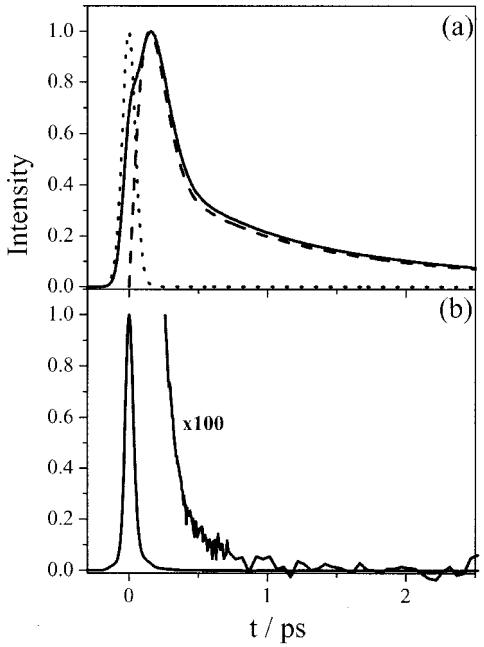

FIG. 1. The measured response of pure CS_2. The OHD-Kerr signal (a) is shown in full line together with the nuclear response (long-dashed) and the pure electronic response (dashed line). This is the anisotropic part of the stimulated Raman response. The transient grating signal (b) was measured employing a probe pulse with polarization at magic angle compared to the pump pulses. The electronic response dominates the weak nuclear response that is also shown with a magnification of a factor of 100. This is the isotropic part of the stimulated Raman response.

In the anisotropic OHD-Kerr experiment, the relaxation time in pure CS_2 is found to be 1.72 ps. Others have reported values of 1.70 ps,[10,11] 1.65 ps,[2] and 1.61 ps[1,6], which are all comparable to the decay rate measured here. The MD simulation yielded a decay rate of 1.44 ps. The difference between the experimental and calculated realignment relaxation times is due to a slightly lower diffusion rate in the modeled liquid[35] than in the experiment, and to some extent to the noise in the tail of the calculated response.

The observed diffusional decay times at delays larger than 2 ps are listed in Table II. It is seen that the reorientational relaxation time of the carbon disulfide molecules is decreasing upon dilution with pentane, relatively constant upon dilution with heptane and increasing when carbon disulfide is diluted with decane. This behavior correlates well with the relative values of the viscosity, listed in Table I. According to the Stokes–Einstein–Debye relation[9] the reorientational relaxation time is

TABLE II. The time constant in ps for the diffusive decay extracted from data after 2 ps (1.5 ps for the MD).

Solvent	100%	70%	50%	30%
Pentane	1.72	1.56	1.48	1.40
Heptane	1.72	1.67	1.68	1.78
Decane	1.72	1.74	1.85	2.03
MD	1.44	1.53	1.41	1.48

$$\tau_D = c\frac{\eta}{kT} + \tau_0, \tag{11}$$

where c is a positive constant. In the MD simulations of the ideal mixtures the relaxation time should be constant. Values between 1.41 and 1.53 ps are found when only considering the data after 1.5 ps. The relative big spread is an indication of the uncertainty due to the fact that the Raman signal intensity in the tail becomes small quite fast.

Many authors have chosen to fit the observed response to phenomenological models of the dynamics. For instance, a sum of diffusional and librational response[2,3,6] was considered, and also a sum of diffusional and interaction induced response.[11] Theoretical investigations[27] show that both librational and interaction induced response are of importance and any model based fit should include both effects to be able to give a correct description of the generation of the Raman signals. Since the same response can be fitted to models ignoring either the librational or the interaction induced response, the physical interpretation of such fits is questionable. When interpreted in terms of the correlation functions given in Eqs. (4)–(9), the diffusional decay and the librational response both belong to the single molecule term Eq. (4), while the interaction induced response is covered by Eqs. (5)–(9).

Experimentally, the relative importance of the single molecule and many-body contributions can, in principle, be inferred from the concentration dependence of the intensity of the Raman response. When the structural, dynamic and chemical effects upon dilution are sufficiently small, only the single molecule term depends linearly on the concentration (see Sec. II). So, fitting the response to a third-order polynomial in the concentration at every delay gives the relative importance of the various terms. In the MD simulations the single molecule term can be found in the same way, but also by simply excluding the DID terms. Comparing the calculated single molecule term found in both ways gives a check on the fitting procedure. In Fig. 2 the linear scaling parts of the third-order responses are shown for the dilution with the three alkanes, together with the linear scaling part of the ideal dilution calculation and the calculated third-order response excluding interaction induced effects.

The linear scaling responses of the experimental solutions are all very similar to each other. The linearly scaling response of the ideal dilution calculations resembles the single molecule response calculated excluding interaction induced effects. However, there is a striking difference between the experimental and the theoretical linear scaling curves of Fig. 2. Examining the normalized Raman responses at various concentrations of CS_2 in Fig. 3 shows

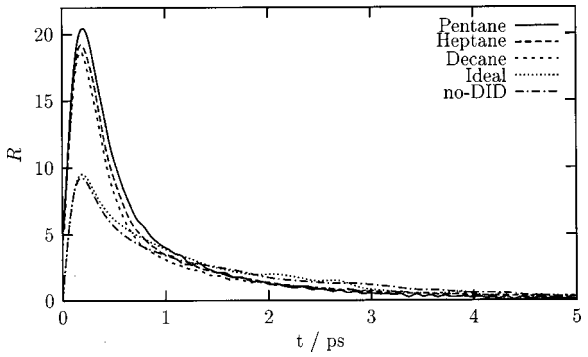

FIG. 2. The linearly scaling part of the anisotropic response found in the three alkanes, from the ideal mixture calculation and from a calculation excluding multibody effects in the polarizability.

little difference between the experiments, whereas the intensity of the peak decreases rapidly compared to the tail upon dilution in the simulated response.

Steffen *et al.*[2] suggested that the almost constant ratio between the initial and the diffusive response upon dilution might be due to the formation of CS_2 aggregates bound together by the big quadrupole moments in CS_2. Larger domains of CS_2 would indeed explain the observed discrepancy between the experiment and calculations. This theory can be tested by adding charges on the chromophore molecules and not on the ghost molecules in order to simulate a mixture of molecules with large quadrupole moments and molecules with no quadrupole moments.

Charges of $-0.308\,e$ on the carbon atoms and $0.154\,e$ on the sulfur atoms were placed on the chromophores in a calculation with 32 chromophore molecules and 32 ghost molecules. The resulting carbon–carbon radial distribution functions are shown in Fig. 4. Only small differences are observed between the chromophore–chromophore, chromophore–ghost, and ghost–ghost radial distribution functions, so aggregation apparently does not occur. The stimulated anisotropic Raman response of this mixture is shown in Fig. 5, showing no difference compared to the result without quadrupole moments.

Another possible explanation for the discrepancy between the simulation of the idealized mixture and the experiment may be found in the fact that all alkanes have densities half the size of the CS_2 density (see Table I). If fluctuations of the density play a role in the initial response, one could imagine that surrounding the chromophores with molecules with lower density enhances the initial response. This could then explain why the initial response is not suppressed experimentally, while it is in the simulation of the idealized mixture, where the density is constant. This idea can be investigated by lowering the mass of the ghost molecules.

Reducing the mass of the ghost molecules from 76.143 g/mol to 58.0716 g/mol and thereby the density of the liquid from 1.26 to 1.09 g/ml when an equal number of chromophore and ghost molecules are present, shows only minor changes in the Raman response as can be seen in Fig. 5. So, the change of the density upon dilution apparently also cannot explain the observed discrepancy between simulation and experiment.

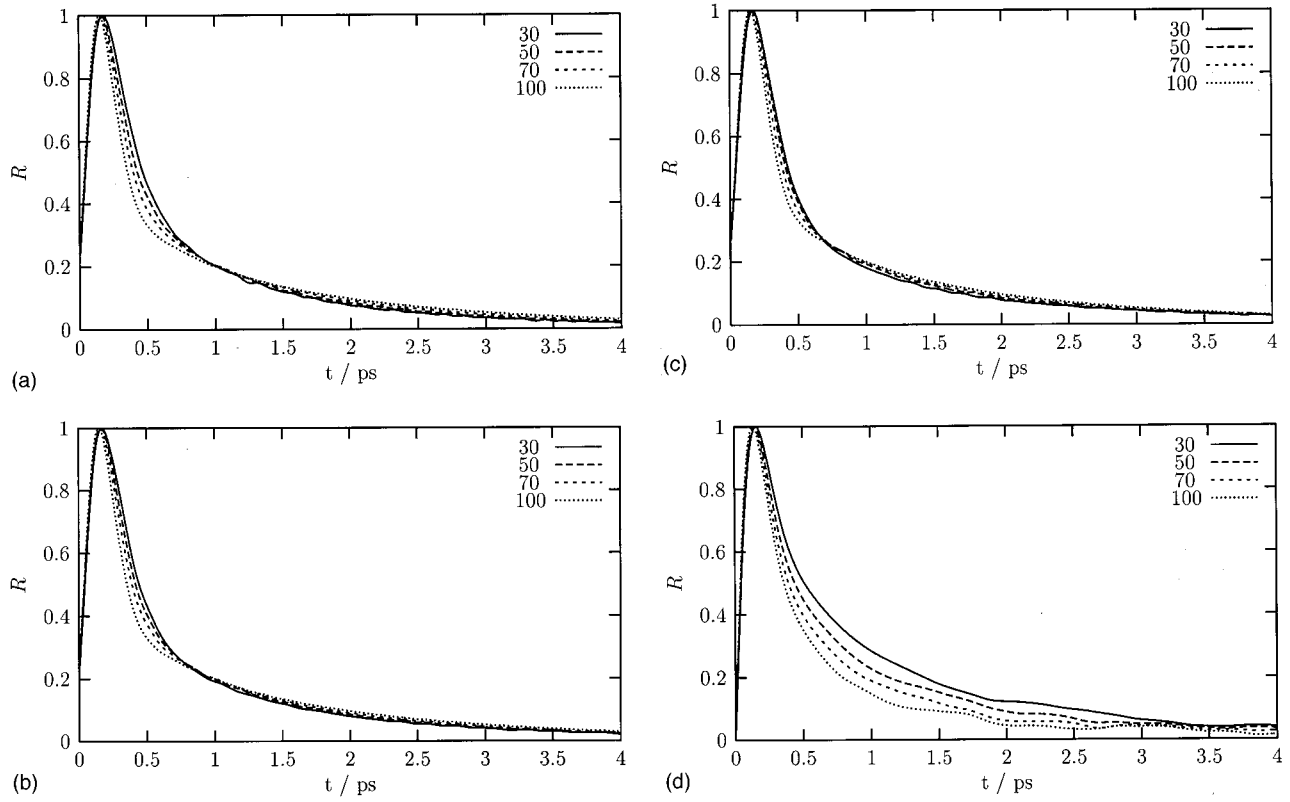

FIG. 3. The normalized CS_2–alkane anisotropic Raman response, measured by OHD Kerr experiments at CS_2 volume fractions of 30%, 50%, 70%, and 100%. (a) Pentane, (b) heptane, (c) decane, and (d) ideal mixture simulation.

The van der Waals interactions between alkane molecules are in general weaker than the intermolecular interactions found in highly polarizable molecules as CS_2. In the CS_2–alkane mixtures the CS_2 molecules can be expected to experience more shallow potentials than in the pure liquid. It is possible that this enhances the librational and interaction induced responses at early times. Varying the depth of the LJ potential on the ghost molecules, can give a clue on the importance of such effects. The presence of more shallow potentials was used previously as an argument to explain the decrease of the maximum in the frequency domain (Fourier transformed) spectrum of the Raman response upon dilution.[2,3,6,7]

Examining the dependence on the force field is rather difficult, since changing the force field will most likely also change the volume of the liquid considerably and hence the volume fraction of CS_2. Furthermore, properties such as the viscosity and the density will also be affected, as is of course also the case in the real experiment. A simulation was performed with a potential depth ϵ of 120 K instead of 183 K on the sulfur atoms in the ghost molecules. The combination rule $\epsilon_{ij}=(\epsilon_{ii}\epsilon_{jj})^{1/2}$ for interactions of these sulfur atoms with the other types of atoms was applied. This mimicks the more shallow potentials expected in alkane mixtures. The

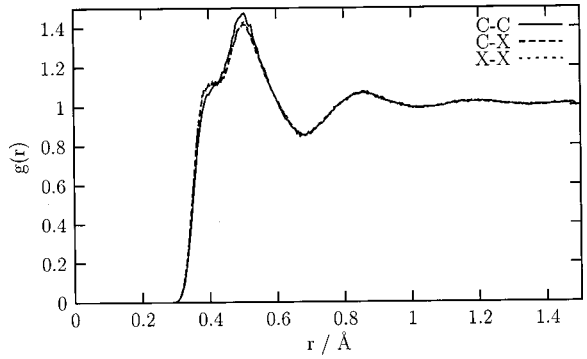

FIG. 4. Radial distribution functions (center of mass) for calculations with chromophores (C) with quadrupole moments and ghost molecules (X) without quadrupole moments.

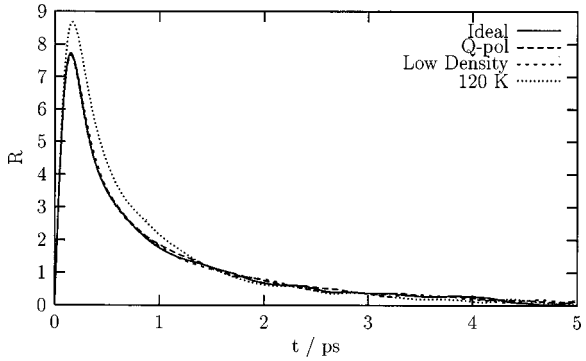

FIG. 5. The calculated anisotropic response of mixtures of 32 chromophores and 32 ghost molecules. The response of an ideal mixture is compared with calculations, where the chromophores have quadrupole moments (Q-pol), where the molecular weight of the ghost molecules is lowered (low density) and where the depth of the LJ potential is reduced from 183 K to 120 K on the ghost molecule sulfur atoms.

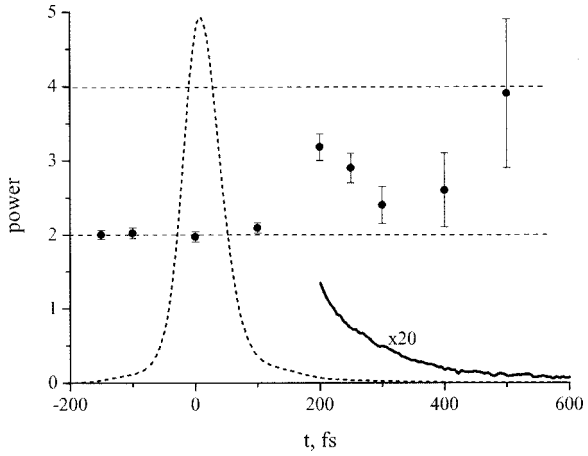

FIG. 6. The power dependence (dots) of the isotropic signal intensity in a mixture of CS_2 and pentane. The electronic signal scales quadratically. A slightly higher power dependence is found in the nuclear part of the response. The response for pure CS_2 is shown as the dotted line, with the nuclear tail also displayed 20 times amplified as the solid line.

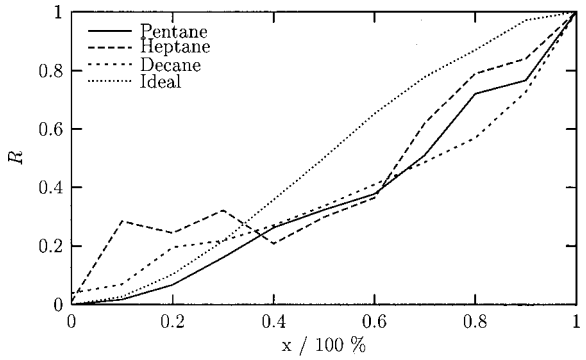

FIG. 7. The concentration dependence isotropic response at 300 fs in the three CS_2–alkane mixtures and in the simulation of an ideal mixture.

volume grows with approximately 10% giving a decrease of the effective volume fraction of CS_2 from 0.5 to 0.457. The simulated response is shown in Fig. 5, where it has been scaled to give approximately the same diffusive tail as the other responses. Now a clear difference is observed compared to the idealized solution calculation. The initial response is stronger even though the volume fraction of CS_2 is lower. This clearly shows that the solvent force field is crucial for the Raman response. Typical potential depths used to describe interactions of CH_3 and CH_2 groups in liquid alkanes are well below 100 K,[36,37] but these could not be applied in the simulations since the ghost molecules would then be similar to the small alkanes ethane and propane. These are both gaseous at room temperature because of their small size.

A general explanation for the deviations between the simulations on the idealized solutions and the experiments could be that the model potentials are not good enough to describe the response. The force field is an atomic LJ model,[33] which has been used for virtually all studies on carbon disulfide. In the present study the molecules are kept rigid and no charges are distributed on the atoms. Other studies[38,39] have included intramolecular motion and charges, but that does not cause any significant change of the low frequency spectrum considered here. Carbon disulfide is a very anisotropic molecule and a high anisotropy can therefore be expected in the van der Waals forces. As also stated in the paper where the LJ model, used here, was first described,[33] a model with isotropic atomic forces cannot describe the anisotropic interactions of a molecule properly at all distances. It will have an isotropic asymptotic behavior in the long distance limit instead of the correct anisotropic asymptotic behavior. However the substantial differences observed between theory and experiment at low concentrations are unlikely to arise from small errors in a model that gives a good description of the pure liquid.

So far, we discussed the concentration dependence of the anisotropic Raman response, i.e., $\chi^{(3)}_{xzxz}$. The isotropic response is about one order of magnitude weaker than the anisotropic one. Since the isotropic response was measured using transient grating scattering, i.e., a homodyne detection technique, the square of the response function is measured and the intensity of the isotropic signal is therefore about two orders of magnitude weaker than the anisotropic signal measured with the same technique. This unfortunately leads to far bigger uncertainties in the experimental results.

The isotropic response contains no contributions from single molecule effects. So, if the mixture is behaving as in the idealized simulations, the isotropic response contains quadratic and cubic scaling terms due to interaction induced contributions, but no linearly scaling terms. The power dependence in the volume fraction of the measured signal is shown in Fig. 6 together with the measured signal for pure CS_2. At short delay times, where the electronic response dominates, the intensity is growing with the second power in the volume fraction. Since this is a homodyne experiment, in which the square of the response function is measured, this indicates that the electronic response is predominantly a single molecule property, depending on the number of CS_2 molecules present in the mixture. At longer delay times (>200 fs), where the nuclear response is expected to dominate the response, the power dependence of the measured signal is clearly larger than 2; it reaches a value around 3. In the theory section it was shown that the interaction-induced nuclear response is expected to grow at least quadratically in the volume fraction and the measured intensity therefore has to show at least fourth and higher-order power dependence. The fact that this is not seen here shows that a mixture of different power dependences on the concentration is present. This means that not only two-body interactions in the first-order susceptibility are important but also other many-body interactions. Fitting to one power is therefore too simple.

In Fig. 7 the concentration dependence of the nuclear isotropic response (square root of the signal intensity) is shown at 300 fs, where the electronic response is expected to have vanished completely. Within the precision of the experiment the behavior of the different CS_2 alkane mixtures are the same. The behavior of the simulated response seems to overestimate the response at high CS_2 fractions. If CS_2 aggregates were formed in the liquid one would expect the opposite effect, i.e., slower disappearance of the multibody isotropic response than predicted by simulations on the ideal mixture.

V. CONCLUSIONS

In this study the anisotropic and isotropic third-order Raman responses have been measured for mixtures of carbon disulfide with a series of alkanes. The experimental results were compared with molecular dynamics simulations of different model mixtures. Significant differences were found between the simplest model and the experiments in the subpicosecond regime. The initial response does not disappear as fast as predicted by the theoretical calculations. Using molecular dynamics we examined some of the possible microscopic explanations for the peculiar deviations. We succeeded in ruling out both aggregation due to large quadrupole moments on carbon disulfide and density fluctuations in the inhomogeneous medium as sources of the discrepancies. In contrast, the shallowness of the potentials found in alkanes could provide a convincing explanation, as shown by the model calculations. The shallow potentials are probably leading to an increase of the librational response at a rate that compensates for the decrease of the interaction-induced response, when diluting. Intramolecular solvent vibrations and the lack of a true anisotropic potential for carbon disulfide cannot be ruled out completely as partial explanations of the differences, since only rigid molecules have been used in the simulations. Further investigations with systematic variations of solvent potentials and vibrational degrees of freedom will be needed to get a more detailed microscopic picture of the response.

We showed that the isotropic response is measurable and reveals important information about the interaction induced response. Also in the isotropic response deviations were observed between the theory and experiments. In contrast to the initial anisotropic response, the isotropic response seems to disappear faster upon dilution in the high concentration limit than predicted by the simulations, which again provides strong evidence against the formation of aggregates. Further studies of the isotropic response should provide more information about the nature of the intermolecular motion and interaction-induced effects in the third-order Raman response.

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